

# Efficient Extraction of U(VI) Ions from Solutions

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**Abstract.** The rapid development of advanced techniques for selective and efficient U(VI) extraction from aqueous solutions is essential for addressing U(VI) environmental pollution and energy issues. Here, we share recent progress in U(VI) extraction from aqueous solutions, especially the most frequently applied techniques such as adsorption, catalysis (photocatalysis, piezocatalysis, and electrocatalysis), chemical deposition, and reduction by zero-valent metal particles. We attempt to elucidate the strategies and various mechanisms that contribute to the enhancement of selective U(VI) extraction. At the end of our review, we highlight the outlook, challenges, and prospects for the development of this field.

**Keywords:** Uranium extraction; Adsorption; Catalysis; Reduction; Chemical deposition

## 1. Introduction

The use of conventional energy sources has gradually caused changes in climate and resulted in an energy crisis, which has caused significant uncertainty recently. Therefore, the development of clean energy, for example, nuclear energy, shows promise for addressing energy and environmental problems. However, the development of nuclear energy relies heavily on the use of uranium as a nuclear fuel [1]. Large quantities of uranium are consumed in the operation of nuclear power stations. The uranium reserve on land (~4.5 to 10 million tons) is estimated to be only 1/500 to 1/1000 that in the sea [2–4]. Consequently, the efficient and selective

extraction of U(VI) from natural seawater is essential to the long-term utilization of nuclear energy [5–9]. In addition, the use of uranium results in the discharge or accidental release of U-containing wastewater into the environment and thus causes environmental disruption and the waste of resources. The efficient extraction/solidification of radionuclides [10–12] is highly important for the management of environmental pollution by radionuclides. In particular, the extraction of uranium from solutions promotes both environmental protection and the safe supply of nuclear fuel.

Under natural conditions, uranium is usually present in valence states III, IV, V, and VI, where U(VI) is the most common form [13]. U(VI) ions are typically soluble and are present mainly as  $\text{UO}_2^{2+}$ ; thus, they migrate easily and are the most toxic U ions. Therefore, most studies of the removal and recycling of U(VI) have focused on how to immobilize U(VI) in solution, and many research groups have developed commonly used methods in this field, including membrane separation, adsorption, evaporation, and reduction [14–17]. The recovery of U(VI) not only has potential for applications in the treatment of environmental pollution but also may alleviate the energy shortage, which has attracted considerable research attention in recent years [18, 19]. Despite great efforts and significant progress, it is still necessary to enhance the efficiency and selectivity of uranium extraction from complicated systems, and new techniques are still urgently needed but challenging to develop.

To efficiently and selectively extract U(VI) ions from aqueous solution, our research group has focused on several conventional techniques including adsorption, photocatalysis, and reduction. Our goal is to design new and highly efficient adsorbents, photocatalysts, and reductants for U(VI) extraction and demonstrate the underlying mechanisms, which may guide real applications. We also developed promising new techniques, for example, piezocatalysis, chemical deposition, and electrocatalysis, and synthesized meticulously designed piezocatalysts and electrocatalysts. These works reported on methods of enhancing U(VI) extraction and systematically demonstrated the superior performance of these methods. Here, we share recent representative works related to U(VI) extraction, mainly those by our

research group and several groups from Hainan University and Soochow University. We hope these works inspire further development of efficient methods of U(VI) extraction from aqueous solutions.

## 2. Extraction of U(VI) from aqueous solutions

### 2.1. Adsorption extraction of U(VI)

Adsorption is a well-established technique for uranium removal and recovery from solutions. This method is dominant because of its high efficiency, cost-effectiveness, easy operability, low sludge production, and suitability for large-scale application. Although adsorption technology has been used in uranium extraction in recent decades on a much wider scale than other methods, many new materials with desirable features, including metallic oxides [20], layered inorganic materials [21, 22], covalent organic frameworks (COFs) [17, 23–25], metal–organic frameworks (MOFs) [26–28], and biomass carbon materials [29–32], have been developed. Their emergence signals a new era in uranium adsorption with high selectivity, capability, and stability.

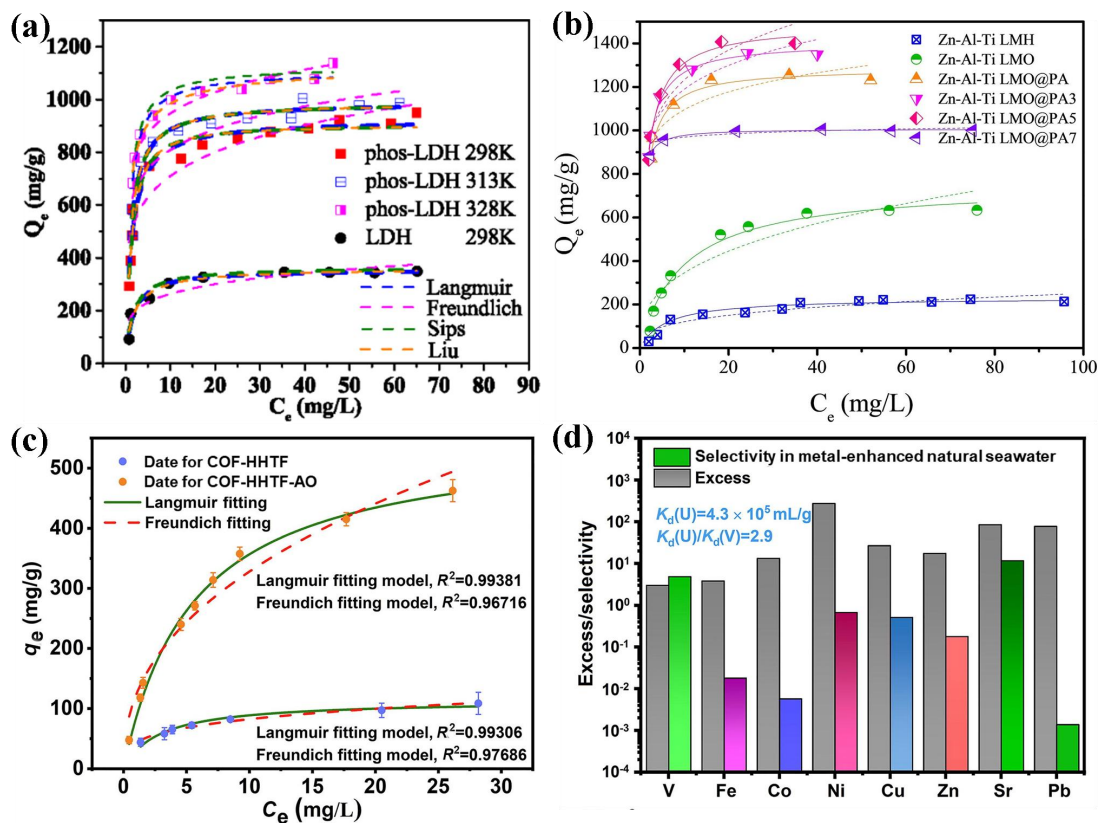
Layered doubled hydroxides (LDHs), with a positively charged layered structure and exchangeable counterions between layers, are highly representative two-dimensional (2D) inorganic cationic framework materials. LDHs are considered to be promising adsorption materials because of their intrinsic features of large surface area, good hydrophilicity, high anion-exchange ability, and excellent surface modifiability. Wang et al. [21] and Cai et al. [22] assembled 2D LDHs with functional P–O ligands with high binding affinity for U(VI) by simple and effective chemical modification routes. The obtained LDH-based materials had maximum adsorption capacities for uranium ( $q_{\max}$ ) of 923.1 and 1486 mg/g, respectively [Figs. 1(a) and 1(b)]. Owing to the abundant active adsorption sites and functional groups of the materials, the adsorption processes exhibited ultrafast kinetics and high selectivity. The predominant adsorption mechanism was identified as strong surface complexation between U(VI) ions and functional groups, which was the main contributor to the high sorption capacity.

MOFs are well-known to have exceptionally high surface areas, highly adjustable pore sizes, and modifiable internal surface properties [33]. Thus, various

MOFs and their derivatives have been successfully synthesized and applied in U(VI) adsorption by our group [34]. For example, rod-like MOF-5 was fabricated by a simple solvothermal process [35] and exhibited a  $q_{\max}$  value for U(VI) of 237.0 mg/g at pH 5.0. The adsorption process appeared to be strongly influenced by pH and weakly influenced by the salt concentration, indicating that interactions between MOF-5 and U(VI) were controlled primarily by electrostatic interaction and inner-sphere complexation, rather than outer-sphere surface complexation. However, pristine MOFs with simple construction usually lack very strong and specific uranium capture sites. Their adsorption properties can be optimized by introducing or tailoring functional groups or components with high affinity for uranium ions on open metal sites or in pore structures [36]. In another work, a magnetic MOF modified by amine groups (Mag MOF-NH<sub>2</sub>) was prepared and used to promote U(VI) extraction from wastewater [37]. At an initial U(VI) concentration of 10 ppm, Mag MOF-NH<sub>2</sub> exhibited an uptake of 80 mg/g within 15 min. The improved adsorption capability compared to that of pristine MIL-101 can be ascribed to the complexation of –NH<sub>2</sub> groups with U(VI) ions. Mag MOF-NH<sub>2</sub> exhibited excellent reusability and high stability for U(VI) removal, where the adsorption efficacy decreased by only ~2% after five cycles of use. In addition, the uranium adsorption performance of Mag MOF-NH<sub>2</sub> in simulated wastewater containing 548 ppm of Ca, 47 ppm of Mg, 4.6 ppm of Al, 0.08 ppm of Co, 0.7 ppm of Ni, and 0.9 ppm of U at pH 5.14 was also investigated; the average adsorption efficiency was 98.43%. These works suggest that MOFs and MOF-based derivatives have excellent prospects for use in the facile separation, preconcentration, and extraction of U(VI) ions from aqueous solution.

COFs are valued for their low mass density, desirable chemical stability, high surface area, permanent porosity, regular pore structure, and facile functional design; they have also attracted significant attention for U(VI) extraction [38]. The introduction of amidoxime groups into COFs can greatly improve their ability to extract uranium, especially from seawater. The pH of seawater is generally accepted to be ~8.2 or ~8.3, and uranium is present at an ultralow concentration of ~3.3 ppb, mainly in the form of uranyl tricarbonatate ([UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>]<sup>4-</sup>) under these conditions [39–41]. In light of this information, Cheng et al. designed and synthesized a COF based on polyarylether and significantly modified with amidoxime (COF-HHTF-AO)

[17], which exhibited impressive chemical stability, as it retained its dioxin linkages and crystal structure after immersion in 14 M NaOH, 12 M HCl, or real seawater for one week. The calculated  $q_{\max}$  values of U(VI) sorption by COF-HHTF-AO and COF-HHTF were 550 and 114 mg/g, respectively [Fig. 1(c)], indicating the importance of amidoxime functionalization. Furthermore, the selectivity of COF-HHTF-AO for U(VI) extraction was 2.9 times that for V(V) extraction. After 25 days of treatment in natural seawater, the sorption ability of COF-HHTF-AO for U(VI) was 5.12 mg/g, which was 1.6 times that for V(V) [Fig. 1(d)]. It is well known that the properties of V(V) are very similar to those of U(VI) in real seawater, and the V(V) concentration is much higher than the U(VI) concentration. Therefore, selective U(VI) extraction is most important for U(VI) preconcentration from real seawater. According to the results of density functional theory calculations, the six-coordinate structure of  $\text{UO}_2^{2+}$  bound to two carbonate and amidoxime groups [ $\text{COF-UO}_2\text{-(CO}_3\text{)}_2$ ] had a higher adsorption energy ( $-19.378$  kcal/mol) than  $\text{HVO}_4^{2-}$  bound with amidoxime ( $-17.080$  kcal/mol). Because of the rigid COF skeleton, COF-HHTF-AO had satisfactory reusability, specificity, and stability for efficient uranium extraction from real seawater, and the adsorption efficiency was 82.4% of the initial efficiency after five adsorption/desorption cycles.



**Fig.1** a Sorption isotherms of U(VI) onto phos-LDH and LDH [21]; b effect of initial U(VI) concentration on U(VI) uptake to Zn–Al–Ti layered metal oxide (LMO), Zn–Al–Ti LMH, and Zn–Al–Ti LMO@phytic acid (PA) [22]; c adsorption isotherms of COF-HHTF-AO and COF-HHTF for U(VI) [17]; d selectivity of U(VI) extraction by COF-HHTF-AO. The selectivity is 100 times that for coexisting metal ions in natural seawater [17].

## 2.2. Catalytic extraction of U(VI)

The soluble form of uranium is usually hexavalent U(VI), which is the highest valence state of uranium. However, some insoluble solids, for example,  $\text{UO}_2$ ,  $\text{U}_3\text{O}_8$ , and  $(\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ , have low migration ability and low toxicity. The most common catalytic solidification process is the reduction of U(VI) from hexavalent U(VI) to tetravalent U(IV) (usually  $\text{UO}_2$ ), and the change from high-valent U(VI) to low-valent U(IV) may greatly decrease the toxicity and facilitate collection. In this process, uranium gains electrons; in theory, if a process can provide electrons to U(VI), a solid

low-valence uranium-containing product can be obtained. Therefore, we developed three catalytic strategies, photocatalysis, piezocatalysis, and electrocatalysis, for the efficient separation, extraction, and solidification of U(VI) in aqueous solutions. Photocatalysis is widely used to treat environmental pollution [42–45] and has exhibited excellent potential for use in U(VI) extraction in recent years [46–48]. By contrast, piezocatalysis is a recently developed strategy for environmental pollution treatment; it is based on the separation of charges by tiny vibrations in non-centrosymmetric crystals [49]. Electrocatalysis utilizes electrons generated by an electric current at the solid–liquid interface to reduce U(VI). In the following sections, we give examples of the catalytic extraction of U(VI) and describe our recent investigation of the charge transfer mechanism in U(VI) reduction.

### 2.2.1. Photocatalytic reduction of U(VI)

Photocatalysis has been studied for several decades and has been increasingly applied in environmental pollution control and energy conversion [42–45]. The photocatalytic reduction of U(VI) has attracted great attention in recent years. The photocatalytic extraction of U(VI) faces two bottlenecks: (1) the design of a highly efficient photocatalyst and (2) inadequate knowledge of the mechanism by which high-valent soluble U(VI) is transformed to the insoluble low-valent U-containing product. To overcome the first bottleneck, in 2019 we designed a graphene-oxide-hybridized  $\text{K}_2\text{Ti}_6\text{O}_{13}$  nanophotocatalyst for efficient and enhanced uranium extraction, where U(VI) in water was totally photoreduced to U(IV) in 120 min [50]. Next, a ternary catalyst,  $\text{CdS}/\text{SnO}_2/\text{CdCO}_3$ , was designed for photocatalytic U(VI) extraction based on electron transfer from CdS to  $\text{SnO}_2$  and  $\text{CdCO}_3$  [42]. This work demonstrated the mechanism of separation and transfer and the final destination of photoelectrons and holes; it offered a highly effective way to recover U(VI) from solution by a photocorrosion-assisted photocatalytic process [Fig. 2(a)]. Inorganic photocatalysts clearly exhibited the advantages of high stability, high capacity, efficient separation of photogenerated electrons and holes, and high visible light absorption. However, the development of novel photocatalysts, in particular MOFs or COFs, has attracted much attention for the photocatalytic reduction of U(VI) because

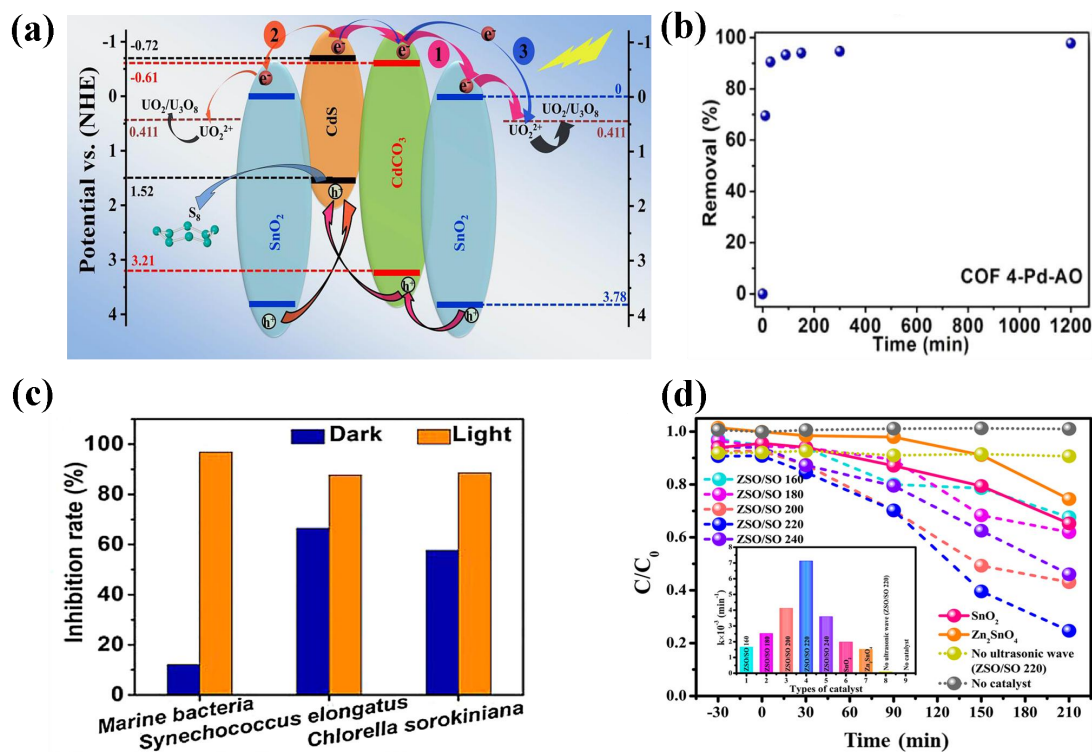


of their strong configurability originating from the versatile components. The use of different components to construct COFs may endow them with additional functions, for example, enhanced adsorption capacity as well as photocatalysis. A novel COF-based hybrid material (COF 4-Pd-AO) containing abundant amidoxime groups and specific photoactive sites reportedly achieved highly efficient uranium extraction by adsorption and photocatalysis [24]. COF 4-Pd-AO performed very well in U(VI) extraction separation under visible sunlight irradiation, as 90% and 94% of the U(VI) was captured within 30 and 90 min, respectively, in seawater spiked with ~25 ppb uranyl [Fig. 2(b)]. The calculated uranium uptake from natural seawater was 4.62 mg/(g · day). The product,  $\text{UO}_2(\text{s})$ , is easily collected, and the triazine groups and bipyridine-Pd(II) constituents of the COF 4-Pd-AO served as dual photocatalytic active sites and generated free radicals ( $\text{O}_2^{\bullet-}$  and  $^1\text{O}_2$ ) under visible light irradiation. Consequently, the COF had antifouling properties because bacterial cell membranes were destroyed [Fig. 2(c)]. The resulting bacterial inactivation ensured easy interaction between U(VI) and the accessible binding sites of COF 4-Pd-AO and reduced the effect of bacteria on the extraction separation of U(VI) from real seawater.

In addition to the development of highly efficient photocatalysis in the presence of photocatalysts, the photocatalytic enrichment of U(VI) in the absence of photocatalysts has also been investigated. At a given pH in the presence of alcohols, a brown uranium product was obtained under visible sunlight irradiation. A theoretical simulation suggested that the catalytic reduction of hexavalent U(VI) to unstable pentavalent U(V) is attributable to ligand-to-metal charge transfer, which can also further reduce U(VI) to U(IV) [51]. In another case, when methanol was added to the catalytic system, the extraction of U(VI) under visible sunlight irradiation was ascribed to the production of  $\text{H}_2\text{O}_2$ , which further reacted with U(VI) to form insoluble uranium peroxide [52]. These two works proposed a facile method of U(VI) extraction. According to the studies described above, the adsorption and photocatalytic reduction of U(VI) using a suitable catalyst is highly effective for extracting U(VI) from complicated solutions. The photocatalytic reduction of U(VI)



under visible sunlight irradiation without a catalyst can also reduce soluble U(VI) to insoluble U(IV) products under appropriate conditions, which also explains the in-situ photocatalytic solidification of uranium under natural environmental conditions.



**Fig.2** **a** The  $e^-h^+$  transfer mechanism during photocatalysis [42]; **b** kinetics of U(VI) sorption on COF 4-Pd-AO at an initial U(VI) concentration of  $\sim 25$  ppb in uranyl-spiked seawater [24]; **c** antibiofouling properties of COF 4-Pd-AO [24]; **d** piezocatalytic properties of  $\text{Zn}_2\text{SnO}_4$ ,  $\text{SnO}_2$ , and ZSO/SO 160–240 for U(VI) removal, with removal rate constants (inset) [16].

### 2.2.2. Piezocatalytic reduction of U(VI)

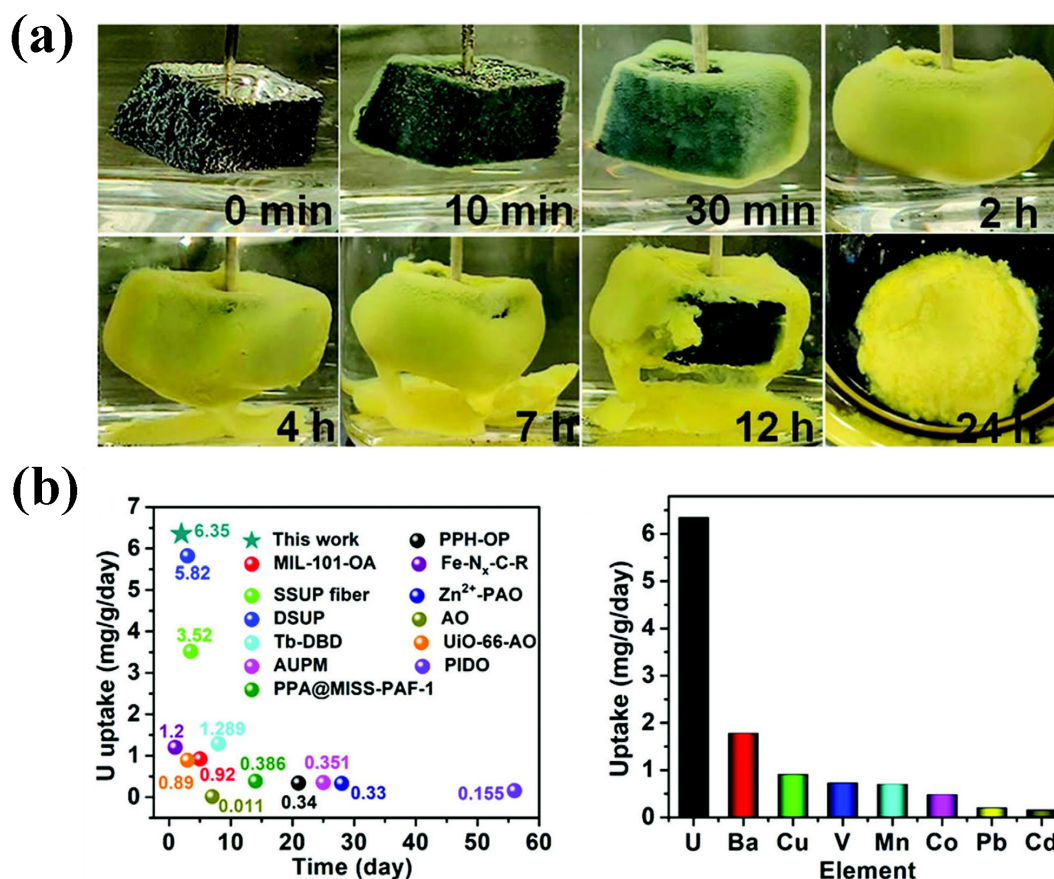
Although the photocatalytic reduction of U(VI) by solar irradiation has recently attracted research attention, the photocatalyst is typically less efficient on cloudy days and at night. In contrast with photocatalysis, piezocatalysis is a new and efficient method that has been developed for several years, especially for environmental and energy applications [49]. Piezocatalysis uses the energy from tiny vibrations caused by, for example, the impacts of raindrops and shaking or bending by wind. These tiny

vibrations can separate the centers of positive and negative charges in some materials with non-centrosymmetric crystal lattices, generating charged surfaces. Molecules or ions on these surfaces may be reduced or oxidized. We presented the first attempt to apply piezocatalysis to the extraction of U(VI) from aqueous solution [16]. In this work,  $\text{Zn}_2\text{SnO}_4/\text{SnO}_2$  nanocomposites with a hollow cubic structure were fabricated for use as a piezocatalyst [Fig. 2(d)]. Under mechanical vibration, the piezo-induced electrons reduced U(VI) adsorbed on the surface to U(IV) ( $\text{UO}_2$ ) and then oxidized the  $\text{UO}_2$  to a solid product,  $(\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ , using  $\text{H}_2\text{O}_2$ . The  $\text{H}_2\text{O}_2$  was produced by the two-step reduction of soluble oxygen; the  $\text{O}_2$  was first reduced by the piezogenerated electrons ( $\text{e}^-$ ) to form  $\cdot\text{O}_2^-$ , and the  $\cdot\text{O}_2^-$  then reacted with  $\text{e}^-$  and  $\text{H}^+$  to produce  $\text{H}_2\text{O}_2$ . Although the U in  $(\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O}$  is still in the hexavalent state, the peroxide is insoluble in water, and thus the product is easily separated from water. This work proposed a new strategy for trapping U(VI) from aqueous solutions in the dark, which does not rely on light irradiation and would have wide applicability in uranium extraction without the use of sunlight and in environmental pollution treatment and energy conversion.

### 2.2.3. Electrocatalytic reduction of U(VI)

Electrocatalysis can accelerate the transfer and reaction of carriers. Our group recently designed a functionalized  $\text{Fe-N}_x\text{-C-R}$  electrocatalyst, where R represents modified amidoxime groups [Fig. 3(a)]. The surface amidoxime groups endowed the  $\text{Fe-N}_x\text{-C-R}$  electrocatalyst with hydrophilicity and could also enhance the adsorption capacity of  $\text{UO}_2^{2+}$  by surface-specific binding. Under an electric field, this electrocatalyst reduced the surface-captured U(VI) to unstable U(V) at the active  $\text{Fe(II)N}_4$  sites. Next, the susceptible  $\text{UO}_2^+$  was re-oxidized to form  $\text{Na}_2\text{O}(\text{UO}_3 \cdot \text{H}_2\text{O})_x$  through the  $\text{Fe(III)N}_4$  center in the presence of  $\text{Na}^+$ . The U(VI) extraction rate in spiked seawater was 1.2 mg/g in 24 h, which is highly efficient compared to those of other processes. In addition, because of the modification and the characteristics of electrocatalysis, this strategy exhibited high selectivity for U(VI) extraction compared to the extraction of vanadium and other competing metal ions in seawater [53]. This work motivated the fabrication of  $\text{In-N}_x\text{-C-R}$  nanocomposites for high-performance

U(VI) extraction from water by electrocatalysis [Fig. 3(b)]; they had an extraction capacity of 6.35 mg/(g·day). The extraction capacity for U(VI) was 8.75 times that for vanadium, indicating superior selectivity for trapping U(VI) from seawater in real applications. The final product of this method is also  $\text{Na}_2\text{O}(\text{UO}_3 \cdot \text{H}_2\text{O})_x$ , and the cost of uranium extraction by this strategy is calculated to be USD 806 per kilogram [54]. To further characterize the formation of  $\text{Na}_2\text{O}(\text{UO}_3 \cdot \text{H}_2\text{O})_x$ , in-situ Raman spectroscopy was used during sorption and electrocatalysis; the results showed the U(V) signal at a wavenumber of  $810 \text{ cm}^{-1}$ , confirming the formation of pentavalent U(V). From these results, one can speculate that U(VI) was reduced to an intermediate product, U(V), which was subsequently re-oxidized to U(VI) and formed  $\text{Na}_2\text{O}(\text{UO}_3 \cdot \text{H}_2\text{O})_x$  with the participation of  $\text{Na}^+$ . This study provides new inspiration for the adsorption and electrocatalytic extraction of U(VI) from real seawater.



**Fig.3 a** Photographs of Fe-N<sub>x</sub>-C-R electrode in uranium-spiked seawater during electrocatalytic extraction [53]; **b** U(VI) extraction by In-N<sub>x</sub>-C-R and other materials (left); extraction selectivity of U(VI) by In-N<sub>x</sub>-C-R from natural seawater (right) [54].

### 2.3. Chemical deposition of U(VI)

Although various methods have been comprehensively investigated and have shown promise for the extraction, separation, and solidification of U(VI) from aqueous solutions, the demand for inexpensive methods with operational feasibility is still a major concern. We recently demonstrated a highly efficient removal method using a chemical deposition reaction [55], where sodium vanadate (Na<sub>2</sub>V<sub>6</sub>O<sub>16</sub>·2H<sub>2</sub>O) nanobelts were obtained by a hydrothermal technique and used for the enrichment of U(VI) ions in water [Fig. 4(a)]. Interestingly, the sample gradually assembled into a granular morphology that extended the contact time with the solution containing U(VI). Careful investigation revealed that the extraction separation of U(VI) occurred by the chemical reaction of Na<sub>2</sub>V<sub>6</sub>O<sub>16</sub>·2H<sub>2</sub>O nanobelts with U(VI) ion groups to form U<sub>2</sub>V<sub>6</sub>O<sub>21</sub>·15H<sub>2</sub>O. The removal capacity of the Na<sub>2</sub>V<sub>6</sub>O<sub>16</sub>·2H<sub>2</sub>O nanobelts was 930.0 mg/g, and the removal efficacy was 93% under the experimental conditions. Most importantly, we found that chemical deposition is not inhibited by coexisting CO<sub>3</sub><sup>2-</sup>. This phenomenon enables easier removal of U(VI).

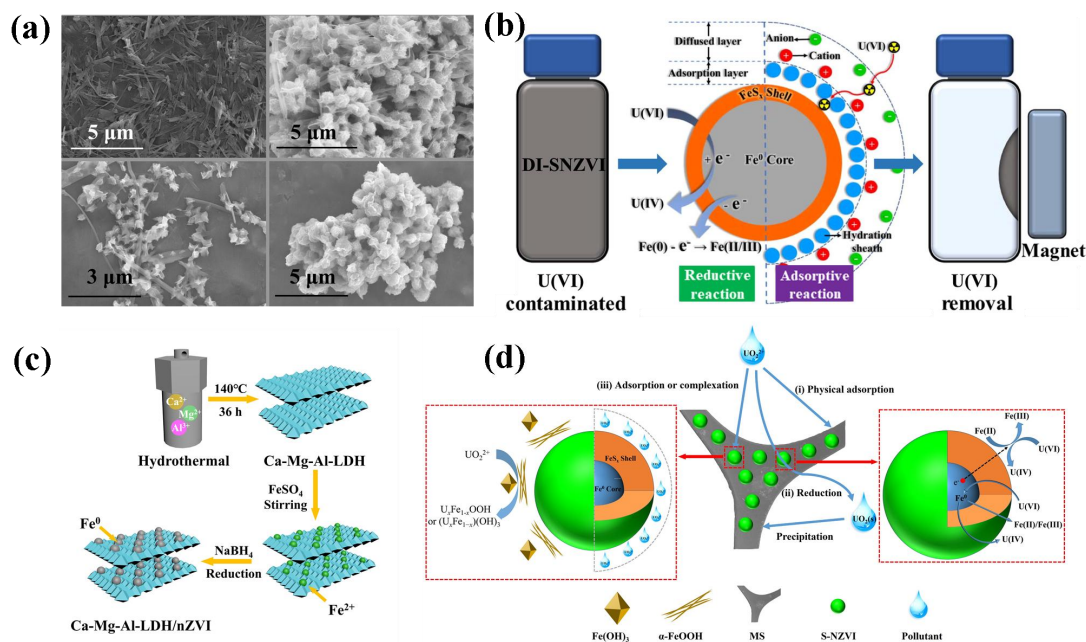
### 2.4. Reduction by Fe<sup>0</sup> nanoparticles

U(VI) reduction is also considered to be an effective strategy for recovering uranium from wastewater. Among various reductants, nanoscale zero-valent iron (NZVI) is most prominent because of its high efficiency and low price. Many types of environmental pollution are treated using NZVI as a reductant. However, NZVI is easily aggregated, make it difficult to store and transport and thus reducing its availability. To decrease aggregation and protect the reductant from oxidation, NZVI is usually modified with a layer of organic or inorganic materials [56]. In a recent

work by our group [Fig. 4(b)], NZVI was protected by an  $\text{FeS}_x$  shell using simple sulfidation technology by immersing NZVI in a  $\text{Na}_2\text{S}_2\text{O}_4$  solution [57]. In the adsorption/reduction process, U(VI) is first adsorbed onto the surfaces of the composite and then converted to U(IV) under the reducing effect of the  $\text{Fe}^0$  core. The maximum uranium elimination capacity of this approach was 427.9 mg/g. In addition, because the nanocomposite can be magnetized, it is very easily separated by a magnet after U(VI) extraction.

Another strategy to avoid the aggregation of  $\text{Fe}^0$  nanoparticles is to disperse them on the surfaces of Ca–Mg–Al–LDH to form an adsorption/reduction bifunctional nanohybridizer [Fig. 4(c)] with a Brunauer–Emmett–Teller surface area of approximately 426.8  $\text{m}^2/\text{g}$ . The large surface area and complicated LDH skeleton structure expose large numbers of active functional groups (for example,  $-\text{OH}$  groups) for capturing U(VI) in solution by adsorption or reduction [58]. The modification of  $\text{Fe}^0$  nanoparticles with a sulfide shell or the loading of  $\text{Fe}^0$  on the surface of an LDH may greatly protect the  $\text{Fe}^0$  nanoparticles from corrosion and inhibit aggregation, thus enhancing the extraction of U(VI). Although magnetic  $\text{Fe}^0$  may be collected easily from water, real applications may still face problems such as difficult operation, and the reductant may be challenging to retrieve. The main defect in both of these strategies involves the anchoring of  $\text{Fe}^0$  on another powder, which is difficult to handle in practice. Therefore, we used another method to enhance operability by anchoring  $\text{Fe}^0$  nanoparticles on a melamine sponge [Fig. 4(d)] [59]. The melamine sponge maintained high elasticity even after modification with  $\text{Fe}^0$  nanoparticles. Most importantly, the composite had a fast reaction equilibrium time of 1 h and a high removal efficiency of 180 mg/g. The composite was easily separated from water either by magnetic separation or by using simple tools, for example, tweezers. These works provide new ideas for U(VI) extraction by reduction from complicated solutions.





**Fig.4** **a** Scanning electron microscopy images of  $\text{Na}_2\text{V}_6\text{O}_{16} \cdot 2\text{H}_2\text{O}$  nanobelts before and after the extraction of U(VI) at different concentrations [55]; **b** schematic diagram of U(VI) uptake from wastewater by adsorptive and reductive processes using sulfurized NZVI [57]; **c** schematic illustration of composite preparation [58]; **d** U(VI) removal mechanisms of melamine sponge supported sulfurized NZVI (MS@S-NZVI) [59].

### 3. Conclusion and outlook

The extraction of uranium from aqueous solutions offers an opportunity to solve environmental and energy issues. In recent studies, the extraction of U(VI) by adsorption, photocatalysis, piezocatalysis, metal reduction, and chemical deposition has attracted much attention and exhibited excellent progress. These studies have demonstrated that U(VI) can be recovered by various mechanisms and form different solid products in different ways. The development of these diverse strategies offers references for U(VI) extraction, and these methods have excellent potential for real applications. The U(VI) extraction performance of various techniques usually depends on the material properties, experimental conditions, and solution properties and composition. For the highly efficient extraction separation of U(VI) ions from complex systems, the properties of the materials are the most critical parameter, and

the separation method generally depends on the material properties. Furthermore, the use of two or more techniques in combination will result in more efficient and more feasible uranium extraction. For example, piezocatalysis can theoretically be triggered by various forms of mechanical energy such as sonic waves, wind, tides, and water flow. Therefore, the combination of photocatalysis and piezocatalysis could make the best use of both solar and tidal energy to extract uranium from seawater around the clock, and their combined effects may also facilitate the separation and migration of photo-/piezo-induced charge carriers. In addition, enhanced adsorption in piezocatalysis can ensure sufficient contact between uranium and the piezogenerated charge carriers on the catalyst, which may also significantly improve the uranium extraction efficiency.

However, challenges remain in the development of novel materials and highly efficient strategies. First, facile fabrication methods for novel materials are important, where the cost should also be considered. In this regard, natural materials, or those obtained by post-treatment at low cost, may have excellent application potential. Second, because of the diverse valence states of uranium and the different conditions in real applications, completely different mechanisms are usually involved in the extraction separation of U(VI). The need to understand the underlying mechanism of each method makes this research both valuable and challenging, and this work also provides various possibilities for enhancing the extraction efficiency. In addition, theoretical simulation must be given sufficient attention, as it is a powerful technique for obtaining information that is hard to get experimentally. For example, recent discoveries based on experimental results and theoretical simulations of the coordination chemistry of various ligands or materials with uranium can provide valuable and significant inspiration for the oriented design of advanced materials for highly selective uranium extraction under different environmental conditions.

Overall, the extraction of U(VI) from solutions is highly important for simultaneously solving the environmental problem and energy crisis, which warrant broader concern, in particular, the study of the design and fabrication of new materials, new techniques, and, equally important, the extraction mechanism and capacity. The



development of highly efficient extraction techniques for U(VI) may greatly mitigate challenges to human survival.

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## References

- [1] M.-L. Tan, G.-F. Zhu, Z.-D. Zhang et al., Burnup optimization of once-through molten salt reactors using enriched uranium and thorium. Nucl. Sci. Tech. **33**, 5 (2022). <https://doi.org/10.1007/s41365-022-00995-2>
- [2] D. S. Sholl and R. P. Lively, Seven chemical separations to change the world. Nature **532**, 435-437 (2016). <https://doi.org/10.1038/532435a>
- [3] S. Kushwaha and K. Patel, Catalyst: uranium extraction from seawater, a paradigm shift in resource recovery. Chem **7**, 271-274 (2021). <https://doi.org/10.1016/j.chempr.2021.01.008>
- [4] L. Grancea, M. Mihalasky, M. Fairclough et al., Uranium 2020: Resources, Production and Demand[R]. No. NEA--7551. Organisation for Economic Co-Operation and Development, 2020.
- [5] Q. Yu, Y. Yuan, L. Feng et al., Spidroin-Inspired, High-Strength, Loofah-Shaped Protein Fiber for Capturing Uranium from Seawater. Angew. Chem. Int. Ed. **59**, 15997-16001 (2020). <https://doi.org/10.1002/anie.202007383>
- [6] H. Yang, Y. Liu, Z. Chen et al., Emerging technologies for uranium extraction from seawater. Science China Chem. **65**, 2335-2337 (2022).

<https://doi.org/10.1007/s11426-022-1358-1>

- [7] B. Yan, C. Ma, J. Gao et al., An Ion-Crosslinked Supramolecular Hydrogel for Ultrahigh and Fast Uranium Recovery from Seawater. *Adv. Mater.* **32**, 1906615 (2020). <https://doi.org/10.1002/adma.201906615>
- [8] W. Sun, L. Feng, L. Zhang et al., Amidoxime Group-Anchored Single Cobalt Atoms for Anti-Biofouling during Uranium Extraction from Seawater. *Adv. Sci.*, **9**, 2105008 (2022). <https://doi.org/10.1002/advs.202105008>
- [9] Y. Yuan, Q. Yu, M. Cao et al., Selective extraction of uranium from seawater with biofouling-resistant polymeric peptide. *Nat. Sustain.* **4**, 708-714 (2021). <https://doi.org/10.1038/s41893-021-00709-3>
- [10] X. Liu, A. Zhang, R. Ma et al., Experimental and theoretical insights into copper phthalocyanine-based covalent organic frameworks for highly efficient radioactive iodine capture. *Chinese Chem. Lett.* **33**, 3549-3555 (2022). <https://doi.org/10.1016/j.cclet.2022.03.001>
- [11] J. Li, B. Li, N. Shen et al., Task-Specific Tailored Cationic Polymeric Network with High Base-Resistance for Unprecedented  $^{99}\text{TcO}_4^-$  Cleanup from Alkaline Nuclear Waste. *ACS Cent. Sci.* **7**, 1441-1450 (2021). <https://doi.org/10.1021/acscentsci.1c00847>
- [12] Y. Wang, S. Hu, L. Cheng et al., Stabilization of Plutonium(V) Within a Crown Ether Inclusion Complex. *CCS Chem.* **2**, 425-431 (2020). <https://doi.org/10.31635/ccschem.020.202000152>
- [13] T. Chen, K. Yu, C. Dong et al. Advanced photocatalysts for uranium extraction: Elaborate design and future perspectives. *Coordin. Chem. Rev.* **467**, 214615 (2022). <https://doi.org/10.1016/j.ccr.2022.214615>
- [14] Y. Zhang, H. Liu, F. Gao et al., Application of MOFs and COFs for photocatalysis in  $\text{CO}_2$  reduction,  $\text{H}_2$  generation, and environmental treatment. *EnergyChem* **4**, 100078 (2022). <https://doi.org/10.1016/j.enchem.2022.100078>
- [15] X. Liu, G. Verma, Z. Chen et al., Metal-Organic Framework Nanocrystals Derived Hollow Porous Materials: Synthetic Strategies and Emerging Applications. *The Innovation* **3**, 100281 (2022).

<https://doi.org/10.1016/j.xinn.2022.100281>

- [16] Y. Cai, Y. Zhang, Z. Lv et al., Highly efficient uranium extraction by a piezo catalytic reduction-oxidation process. *Appl. Catal. B-Environ.* **310**, 121343 (2022). <https://doi.org/10.1016/j.apcatb.2022.121343>
- [17] G. Cheng, A. Zhang, Z. Zhao et al., Extremely stable amidoxime functionalized covalent organic frameworks for uranium extraction from seawater with high efficiency and selectivity. *Sci. Bull.* **66**, 1994-2001 (2021). <https://doi.org/10.1016/j.scib.2021.05.012>
- [18] L. Xu, J.-T. Hu, H.-J. Ma et al., Amidoxime-based adsorbents prepared by cografting acrylic acid with acrylonitrile onto HDPE fiber for the recovery of uranium from seawater. *Nucl. Sci. Tech.* **28**, 45 (2017). <https://doi.org/10.1007/s41365-017-0198-7>
- [19] X. Xu, X.-J. Ding, J.-X. Ao et al., Preparation of amidoxime-based PE/PP fibers for extraction of uranium from aqueous solution. *Nucl. Sci. Tech.* **30**, 20 (2019). <https://doi.org/10.1007/s41365-019-0543-0>
- [20] Y. Hu, X. Wang, Y. Zou et al., Superior sorption capacities of Ca-Ti and Ca-Al bimetallic oxides for U(VI) from aqueous solutions. *Chem. Eng. J.* **316**, 419-428 (2017). <https://doi.org/10.1016/j.cej.2017.01.115>
- [21] X. Wang, Y. Cai, T. Han et al., Phosphate functionalized layered double hydroxides (phos-LDH) for ultrafast and efficient U(VI) uptake from polluted solutions. *J. Hazard. Mater.* **399**, 123081 (2020). <https://doi.org/10.1016/j.jhazmat.2020.123081>
- [22] Y. Cai, Y. Ma, J. Feng et al., Insight into the performance and mechanism of low-cost phytic acid modified Zn-Al-Ti LMO for U(VI) removal. *Chem. Eng. J.* **402**, 125510 (2020). <https://doi.org/10.1016/j.cej.2020.125510>
- [23] M. Hao, Z. Chen, H. Yang et al., Pyridinium salt-based covalent organic framework with well-defined nanochannels for efficient and selective capture of aqueous  $^{99}\text{TcO}_4^-$ . *Sci. Bull.* **67**, 924-932 (2022). <https://doi.org/10.1016/j.scib.2022.02.012>
- [24] M. Hao, Z. Chen, X. Liu, et al., Converging Cooperative Functions into the

Nanospace of Covalent Organic Frameworks for Efficient Uranium Extraction from Seawater. *CCS Chem.* **4**, 2294-2307 (2022).

<https://doi.org/10.31635/ccschem.022.202201897>

- [25] P. Duan, D.-Y. Lin, W.-T. Yang et al., Facile preparation of covalent organic frameworks@alginate composite beads for enhanced uranium(VI) adsorption. *Rare Met.* **41**, 1323-1331 (2022). <https://doi.org/10.1007/s12598-021-01884-0>
- [26] H. Zhang, W. Liu, A. Li et al., Three Mechanisms in One Material: Uranium Capture by a Polyoxometalate–Organic Framework through Combined Complexation, Chemical Reduction, and Photocatalytic Reduction. *Angew. Chem. Int. Ed.* **58**, 16110-16114 (2019). <https://doi.org/10.1002/anie.201909718>
- [27] H. Zhu, J. Yuan, X. Tan et al., Efficient removal of  $Pb^{2+}$  by Tb-MOFs: identifying the adsorption mechanism through experimental and theoretical investigations. *Environ. Sci.: Nano* **6**, 261-272 (2019). <https://doi.org/10.1039/C8EN01066H>
- [28] W. Yang, Q. Pan, S. Song et al., Metal-organic framework-based materials for the recovery of uranium from aqueous solutions. *Inorg. Chem. Front.* **6**, 1924-1937 (2019). <https://doi.org/10.1039/C9QI00386J>
- [29] X. Wang, J. Feng, Y. Cai et al., Porous biochar modified with polyethyleneimine (PEI) for effective enrichment of U(VI) in aqueous solution. *Sci. Total Environ.* **708**, 134575 (2020). <https://doi.org/10.1016/j.scitotenv.2019.134575>
- [30] H. Chen, Y. Gao, J. Li et al., Engineered biochar for environmental decontamination in aquatic and soil systems: a review. *Carbon Res.* **1**, 4 (2022). <https://doi.org/10.1007/s44246-022-00005-5>
- [31] X. Song, P. Wang, L. Van Zwieten et al., Towards a better understanding of the role of Fe cycling in soil for carbon stabilization and degradation. *Carbon Res.* **1**, 5 (2022). <https://doi.org/10.1007/s44246-022-00008-2>
- [32] Z. Xu, D.C.W. Tsang, Redox-induced transformation of potentially toxic elements with organic carbon in soil. *Carbon Res.* **1**, 9 (2022). <https://doi.org/10.1007/s44246-022-00010-8>
- [33] X. Yang, X. Liu, Y. Liu et al., Optimizing Iodine Capture Performance by Metal-Organic Framework Containing with Bipyridine Units. *Front. Chem. Sci.*

Eng. (2022). <https://doi.org/10.1007/s11705-022-2218-3>

- [34] J. Li, X. Wang, G. Zhao et al., Metal-organic framework-based materials: superior adsorbents for the capture of toxic and radioactive metal ions. *Chem. Soc. Rev.* **47**, 2322-2356 (2018). <https://doi.org/10.1039/C7CS00543A>
- [35] Y. Wu, H. Pang, W. Yao et al., Synthesis of rod-like metal-organic framework (MOF-5) nanomaterial for efficient removal of U(VI): batch experiments and spectroscopy study. *Sci. Bull.* **63**, 831-839 (2018). <https://doi.org/10.1016/j.scib.2018.05.021>
- [36] Z. Zhao, G. Cheng, Y. Zhang et al., Metal-Organic-Framework Based Functional Materials for Uranium Recovery: Performance Optimization and Structure/Functionality-Activity Relationships, *ChemPlusChem* **86**, 1177-1192 (2021). <https://doi.org/10.1002/cplu.202100315>
- [37] W. Chen, Y. Cai, Z. Lv et al., Improvement of U(VI) removal by tuning magnetic metal organic frameworks with amine ligands. *J. Mol. Liq.* **334**, 116495 (2021). <https://doi.org/10.1016/j.molliq.2021.116495>
- [38] Y. Cai, Q. Ling, Y. Yi et al., Application of covalent organic frameworks in environmental pollution management. *Appl. Catal. A-Gen.* **643**, 118733 (2022). <https://doi.org/10.1016/j.apcata.2022.118733>
- [39] G.M. Marion, F.J. Millero, M.F. Camões et al. pH of seawater. *Mar. Chem.* **126**, 89-96 (2011). <https://doi.org/10.1016/j.marchem.2011.04.002>
- [40] C. W. Abney, R. T. Mayes, T. Saito et al., Materials for the Recovery of Uranium from Seawater. *Chem. Rev.* **117**, 13935-14013 (2017). <https://doi.org/10.1021/acs.chemrev.7b00355>
- [41] H. Gu, X. Liu, S. Wang et al. COF-based composites: extraordinary removal performance for heavy metals and radionuclides from aqueous solutions. *Rev. Environ. Contam. Toxicol.* **260**, 23 (2022). <https://doi.org/10.1007/s44169-022-00018-6>
- [42] Y. Zhang, M. Zhu, S. Zhang et al., Highly efficient removal of U(VI) by the photoreduction of SnO<sub>2</sub>/CdCO<sub>3</sub>/CdS nanocomposite under visible light irradiation. *Appl. Catal. B-Environ.* **279**, 119390 (2020).

<https://doi.org/10.1016/j.apcatb.2020.119390>

- [43] L. Yao, Y. Hu, Y. Zou et al., Selective and Efficient Photoextraction of Aqueous Cr(VI) as a Solid-State Polyhydroxy Cr(V) Complex for Environmental Remediation and Resource Recovery. *Environ. Sci. Technol.* **56**, 14030-14037 (2022). <https://doi.org/10.1021/acs.est.2c03994>
- [44] Y. Hu, D. Tang, Z. Shen et al., Photochemically triggered self-extraction of uranium from aqueous solution under ambient conditions. *Appl. Catal. B-Environ.* **322**, 122092 (2023). <https://doi.org/10.1016/j.apcatb.2022.122092>
- [45] L. Yao, Z. Shen, Z. Ji et al., Cr(VI) detoxification and simultaneous selective recovery of Cr resource from wastewater via photo-chemical extraction using biomass. *Sci. Bull.* **67**, 2154-2157 (2022). <https://doi.org/10.1016/j.scib.2022.10.013>
- [46] Z. Liu, Z. Xu, L. Xu et al., Modified biochar: Synthesis and mechanism for removal of environmental heavy metals. *Carbon Res.* **1**, 8 (2022). <https://doi.org/10.1007/s44246-022-00007-3>
- [47] Y. Lu, Y. Cai, L. Zhuang et al., Application of biochar-based photocatalysts for sorption-(photo)degradation/reduction of environmental contaminants: Mechanism, challenges and perspective. *Biochar*, **4**, 45 (2022). <https://doi.org/10.1007/s42773-022-00173-y>
- [48] L. Feng, Y. Yuan, B. Yan et al., Halogen hydrogen-bonded organic framework (XHOF) constructed by singlet open-shell diradical for efficient photoreduction of U(VI). *Nat. Comm.* **13**, 1389 (2022). <https://doi.org/10.1038/s41467-022-29107-9>
- [49] F. Gao, M. Fang, S. Zhang et al., Symmetry-breaking induced piezocatalysis of Bi<sub>2</sub>S<sub>3</sub> nanorods and boosted by alternating magnetic field. *Appl. Catal. B-Environ.* **316**, 121664 (2022). <https://doi.org/10.1016/j.apcatb.2022.121664>
- [50] M. Zhu, Y. Cai, S. Liu et al., K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> Hybridized Graphene Oxide: Effective Enhancement in Photodegradation of RhB and Photoreduction of U(VI). *Environ. Pollut.* **248**, 448-455 (2019). <https://doi.org/10.1016/j.envpol.2019.02.025>
- [51] S. Li, Y. Hu, Z. Shen et al., Rapid and selective uranium extraction from aqueous

solution under visible light in the absence of solid photocatalyst. *Sci. China Chem.* **64**, 1323-1331 (2021). <https://doi.org/10.1007/s11426-021-9987-1>

- [52] Z. Wang, B. Li, H. Shang et al., Photo-induced removal of uranium under air atmosphere without external photocatalyst. *Green Chem.* **24**, 7092-7099 (2022). <https://doi.org/10.1039/D2GC02739A>
- [53] H. Yang, X. Liu, M. Hao et al., Functionalized Iron–Nitrogen–Carbon Electrocatalyst Provides a Reversible Electron Transfer Platform for Efficient Uranium Extraction from Seawater. *Adv. Mater.* **33**, 2106621 (2021). <https://doi.org/10.1002/adma.202106621>
- [54] X. Liu, Y. Xie, M. Hao et al., Highly Efficient Electrocatalytic Uranium Extraction from Seawater over an Amidoxime–Functionalized In–N–C Catalyst. *Adv. Sci.* **9**, 2201735 (2022). <https://doi.org/10.1002/advs.202201735>
- [55] Y. Zhang, Y. Cai, S. Zhang et al., Super-efficient Extraction of U(VI) by the Dual-functional Sodium Vanadate ( $\text{Na}_2\text{V}_6\text{O}_{16} \cdot 2\text{H}_2\text{O}$ ) Nanobelts. *Chem. Eng. J.* **446**, 137230 (2022). <https://doi.org/10.1016/j.cej.2022.137230>
- [56] Z. Chen, X. He, Q. Li et al., Low-temperature plasma induced phosphate groups onto coffee residue-derived porous carbon for efficient U(VI) extraction. *J. Environ. Sci.* **122**, 1-13 (2022). <https://doi.org/10.1016/j.jes.2021.10.003>
- [57] H. Pang, Z. Diao, X. Wang et al., Adsorptive and reductive removal of U(VI) by Dictyophora indusiata-derived biochar supported sulfide NZVI from wastewater. *Chem. Eng. J.* **366**, 368-377 (2019). <https://doi.org/10.1016/j.cej.2019.02.098>
- [58] H. Pang, Y. Wu, S. Huang et al., Macroscopic and microscopic investigation of uranium elimination by Ca–Mg–Al-layered double hydroxide supported nanoscale zero valent iron. *Inorg. Chem. Front.* **5**, 2657-2665 (2018). <https://doi.org/10.1039/C8QI00779A>
- [59] H. Tang, S. Zhang, H. Pang et al., Insights into enhanced removal of U(VI) by melamine sponge supported sulfurized nanoscale zero-valent iron. *J. Clean. Prod.* **329**, 129662 (2021). <https://doi.org/10.1016/j.jclepro.2021.129662>



## Graphical abstract

